

ABSTRACT

The subject of the present invention is a pyrotechnic gas-generating product, the composition of which comprises:

- guanidine nitrate,
- basic copper nitrate, and
- potassium perchlorate.

Characteristically, said potassium perchlorate represents between 8% and 20% of the total weight of said pyrotechnic product and said composition additionally contains at least one oxide, chosen from metal oxides, metalloid oxides and mixtures thereof; said at least one oxide having a melting point below the combustion temperature of said pyrotechnic product and said at least one oxide representing between 1% and 5% of the total weight of said pyrotechnic product. Said at least one oxide improves the combustion, at low pressure, of said pyrotechnic product.

CLAIMS

1. A pyrotechnic gas-generating product, the composition of which comprises:

- guanidine nitrate,
- basic copper nitrate, and
- potassium perchlorate,

characterized in that said potassium perchlorate represents between 8% and 20% of the total weight of said pyrotechnic product; and

said composition additionally contains at least one oxide, chosen from metal oxides, metalloid oxides and mixtures thereof; said at least one oxide representing between 1% and 5% of the total weight of said pyrotechnic product and having a melting point below the combustion temperature of the pyrotechnic product.

2. The product as claimed in claim 1, characterized in that said potassium perchlorate represents between 10.5% and 20% of the total weight of said pyrotechnic product.

3. The product as claimed in claim 1 or 2, characterized in that said melting point of said at least one oxide is at least 50 K below said combustion temperature of said pyrotechnic product.

4. The product as claimed in any one of claims 1 to 3, characterized in that said at least one oxide is chosen from silicon oxide (SiO_2), tungsten oxide (WO_3) and molybdenum oxide (MoO_3).

5. The product as claimed in claim 4, characterized in that said at least one oxide consists of silicon oxide.

6. The product as claimed in any one of claims 1 to 5, characterized in that its composition comprises, expressed as weight percentage:

- from 50% to 65% of guanidine nitrate,

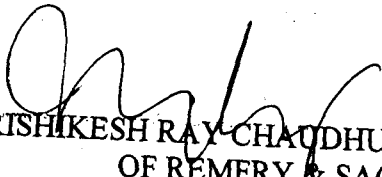
- from 20% to 40% of basic copper nitrate,
- from 8% to 20%, advantageously from 10.5% to 20%, of potassium perchlorate, and
- from 1% to 5%, advantageously from 1% to 3%, of said at least one oxide.

7. The product as claimed in any one of claims 1 to 6, characterized in that it is obtained by a dry process that comprises a step of compacting a pulverulent mixture containing its constituent ingredients as powder, optionally followed by a step of granulation, itself followed, if necessary, by a step of forming via pelletizing.

8. The product as claimed in any one of claims 1 to 7, characterized in that it is in the form of granules, pellets or blocks.

9. A gas generator, suitable for an airbag, characterized in that it contains at least one product as claimed in any one of claims 1 to 8.

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FIG.1

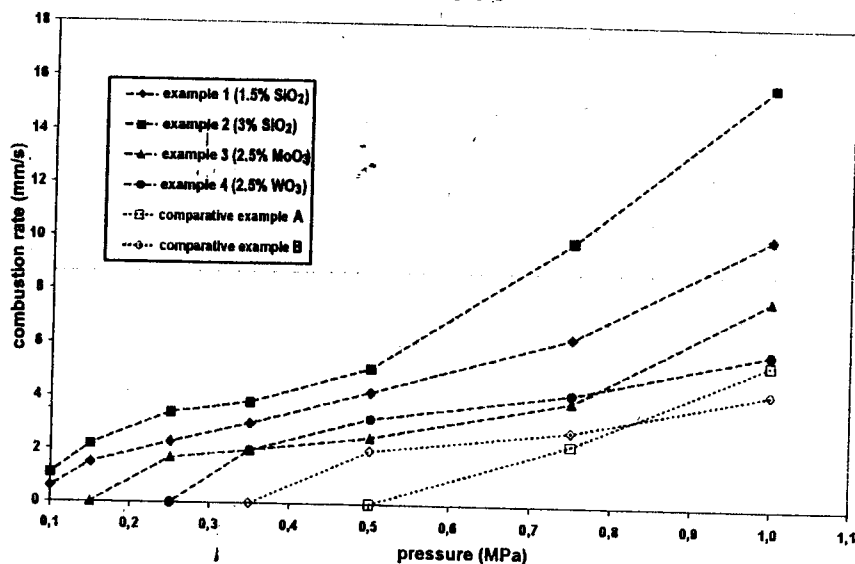
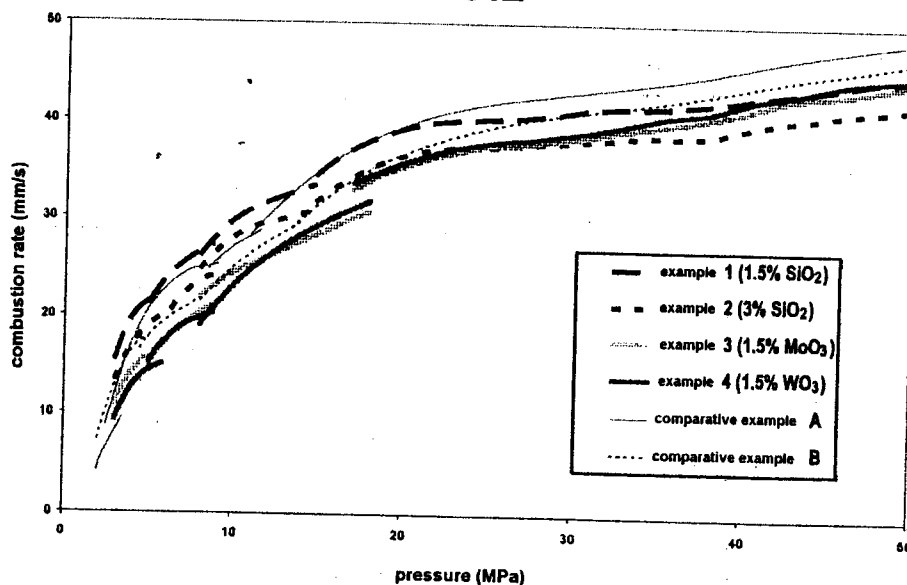
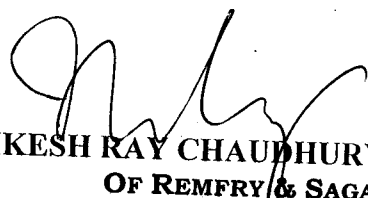


FIG.2




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Gas-generating pyrotechnic products

The present invention relates to pyrotechnic gas-generating products, suitable for use in motor vehicle occupant protection systems, for example for the inflation of airbags or for seatbelt pretensioners.

The technical field relating to motor vehicle occupant protection has experienced a very large expansion over the last twenty years. The latest generation vehicles from now on integrate within the passenger compartment several safety systems, of airbag type or of seatbelt pretensioner type, the operation of which is carried out by the combustion gases of pyrotechnic products. Among the airbag-type systems, airbags for front impact (driver or passenger airbags) and those for side impact (curtain or thorax-protection airbags) are mainly distinguished.

In view of the required reductions in the cost of gas generators for airbags imposed by motor vehicle manufacturers, the pyrotechnic charge must simultaneously satisfy the following requirements:

- the gases generated by the combustion of the pyrotechnic charge must be non-toxic, that is to say have a low content of carbon monoxide, of nitrogen oxides and of chlorinated compounds;
- the gas yield of the composition (that is to say the amount of gas generated by the combustion) must be high in order to lead to a high inflation power. This is given by the product of the molar gas yield of said composition (in mol/kg) and its combustion temperature T_c (in K);
- in a correlated manner, the amount of solid particles generated by the combustion, capable of constituting hot spots that may damage the wall of the airbag, must remain low;
- the combustion temperature must not be too high (ideally less than 2200 K) so that the temperature of the gases in the airbag is low enough to not attack the physical integrity of the occupant. A low combustion temperature makes it possible, on the one hand, to limit the thickness of the bag and, on the other hand, to simplify the design of the gas generator by making it possible to reduce the presence of baffles and filters within this

bag. Finally, the gas generator has a reduced weight and reduced volume, at a lower cost; and

- the pyrotechnic composition must have a high value of the inflation rate per unit area, which rate is estimated by the product $\rho \times n \times T_c \times V_c$, where ρ is the density of the pyrotechnic material (expressed in g/cm^3), n is the molar gas yield of the combustion (expressed in mol/g), T_c is the combustion temperature (expressed in Kelvin) and V_c is the combustion rate (expressed in mm/s). Thus, the parameter of inflation rate per unit area is expressed in $\text{mol.K.mm}^{-2}.\text{s}^{-1}$.

The airbag systems for side application differ from those for front application essentially due to the time required for the deployment and positioning of the airbag. Typically, this time is shorter for a side airbag (of the order of 10-20 ms, compared to 40-50 ms for a front airbag). For a side airbag, the functional requirement of inflation of the bag over a short time makes it necessary to resort to a pyrotechnic composition having a high combustion rate (typically greater than 35 mm/s at 20 MPa and greater than 40 mm/s at 50 MPa) over the entire operating pressure range in the combustion chamber of the generator (typically of the order of 20-80 MPa), in order to obtain a sufficient value of the inflation rate per unit area (product $\rho \times n \times T_c \times V_c$). Furthermore, in order to ensure a satisfactory start-up of the system, the pyrotechnic composition must also have good ignitability characteristics. Lastly, considering the generally tapered surface profile of the charges used (of pellet type), the composition should ideally have a combustion rate that is stable and high enough at low pressure (low pressure is understood to mean a pressure equal to or slightly greater than atmospheric pressure).

Furthermore, the airbag systems for side application may require two gas generator technologies: those which are said to be entirely pyrotechnic (the gas generation then being carried out exclusively by the combustion of a pyrotechnic charge) and those said to be "hybrid" (the gases then originating jointly from the combustion of a pyrotechnic charge and from an inert gas volume stored under pressure in a leaktight reservoir). For "hybrid" generators, the pyrotechnic charge must not have too low a combustion temperature so that the combustion gases are hot enough to compensate for the drop in temperature generated by the

volume expansion of the precompressed inert gas. Ideally, combustion temperatures above 2000 K are required.

Thus, a person skilled in the art is in search of pyrotechnic compositions that simultaneously have a moderate combustion temperature of the order of 2000-2200 K and a high combustion rate over the entire operating pressure range, including at low pressure, so that said compositions are suitable for use in entirely pyrotechnic gas generators or in hybrid generators intended for side airbags.

Various types of pyrotechnic compositions have already been proposed to date. Currently, the pyrotechnic compositions that appear to offer the best compromise in terms of combustion temperature and toxicity of the combustion gases are formulated from the mixture of basic copper nitrate (BCN) as oxidizing charge and guanidine nitrate (GN) as reducing charge. The use of the BCN/GN pair makes it possible to obtain a low combustion temperature, typically of the order of 1800 K. Patent US 5 608 183 describes such compositions, obtained by a wet manufacturing process. However, these compositions have, as major drawbacks:

- a high content of non-filterable solid residues. These residues originate from the decomposition of the BCN, in the form of droplets of liquid copper at the temperature that exists in the combustion chamber of the gas generator, droplets which solidify on leaving said generator. The resulting hot solid particles are then capable of damaging the wall of the airbag;
- a difficult "ignitability" requiring the use of a sizeable ignition charge, which increases the cost of the generator;
- a gas yield that is not very high;
- a too low combustion temperature, which makes it difficult to render their use compatible in "hybrid" generators; and
- a low combustion rate (close to 20 mm/s at 20 MPa), which makes their use in entirely pyrotechnic generators or "hybrid" generators for side airbags difficult.

According to the prior art, it has been proposed, in order to overcome the first of the major drawbacks mentioned above, to incorporate, into the pyrotechnic composition, a refractory oxide such as aluminum oxide or silicon oxide for the purpose of agglomerating the

liquid combustion residues of the BCN. Thus, patent US 6 143 102 describes compositions based on BCN and on GN, still obtained by the wet route, incorporating, as refractory oxide, silicon oxide, at a content which may range up to 5% by weight. A person skilled in the art knows that this agglomeration effect is made possible by the fact that silicon oxide has a melting point (or softening point) of 1950 K, greater than, or at the very least close to, the combustion temperature of the composition $T_c = 1800$ K, so that the softened solid-state oxide makes it possible to agglomerate the droplets of liquid copper. Thus, at the end of the combustion, the backbone of the pyrotechnic block is obtained. However, the incorporation, even at a low content, of such an agglomerating oxide rapidly proves prejudicial to the combustion rate, due to the fact that this agglomeration effect generates a particulate gangue which remains in contact with the pyrotechnic block (of the pellet) during the combustion and which limits the heat flow to the surface not yet burnt. This type of pyrotechnic composition therefore has the drawback of a low combustion rate and a low gas yield. To compensate for said low combustion rate of the compositions described, the incorporation is proposed, in patent US 6 143 102, of a second refractory additive of metal oxide type (aluminum, titanium, zirconium, zinc or magnesium oxide) as ballistic catalyst. Finally, the incorporation of silicon oxide and of a metal oxide, at a total content close to 10% (by weight), is greatly detrimental to the gas yield value of the composition.

To improve the "ignitability" of compositions based on BCN and on GN, the addition of potassium perchlorate to these compositions has been proposed according to the prior art. Patent application EP 1 526 121 thus describes the addition of a perchlorate (in particular potassium perchlorate), at a low content (less than 5% by weight), in order to improve the ignition of said compositions. The incorporation of perchlorate at such a low content makes it possible to slightly increase the combustion rate and the gas yield of the composition, this improvement remaining however insufficient for use in gas generators for side airbags.

Patent application US 2006/0016529 describes compositions based on guanidine nitrate (40% to 60% by weight), on basic copper nitrate (35% to 50% by weight), on alkali metal perchlorate, present at contents which may be higher than those according to the teaching of patent

EP 1 526 121 (1% to 10% by weight) but remaining limited, and on metal oxides (1% to 5% by weight) playing the part of ballistic catalyst and agglomerating agent. Said metal oxides are present for the same agglomeration purposes as according to the teaching of patent US 6 143 102 (see above).

The addition of potassium perchlorate in a larger amount (in an amount that is however limited, that is to say typically less than 30%, so as not to lead to an unacceptable rise in the combustion temperature) results in a notable increase in the gas yield, and also, when it is associated with a particular process for obtaining the product, in a notable increase in the combustion rate. Thus, patent application FR 2 892 117 describes a composition based on guanidine nitrate (reducing agent), on basic copper nitrate (main oxidizing agent) at a reduced content and on potassium perchlorate (co-oxidizing agent) at a higher content, up to 30% by weight. The low content of basic copper nitrate does not require the addition of agglomerating agent to the composition (the small amount of copper particles produced by the BCN being acceptable within the context of the application described), and the high content of potassium perchlorate associated with a specific process for obtaining the product makes it possible to achieve high combustion rates at medium and high pressure that do not require the addition of ballistic catalyst. These compositions constitute the prior art closest to the present invention.

Patent application FR 2 892 117 therefore teaches that the combination of moderate contents of potassium perchlorate (close to 14%), of basic copper nitrate and of a use of a dry compacting process results in pyrotechnic compositions being obtained that advantageously reconcile:

- a combustion temperature close to 2100 K,
- a high combustion rate at high pressure,
- a high gas yield,
- a good "ignitability", and
- a small quantity of solid (copper) particles generated during the combustion, which makes it possible to do away with the presence of an agglomerating agent.

However, this type of composition has a combustion pressure limit which is located above atmospheric pressure. The absence of self-

sustaining combustion at atmospheric pressure, and also a high pressure exponent below 2 MPa, may result, depending on the operating pressure and the geometry of the charge, in extinguishment at the end of combustion. Indeed, a person skilled in the art knows the impact induced by the incorporation of perchlorate, which proves favorable to the combustion rate at high pressure but less favorable to the combustion at very low pressure, once the content of perchlorate incorporated becomes large. At low pressure, the high expansion generated by the high gas yield associated with the low content of solid particles induces a slight return of heat flow to the unburnt zone: this being the case, the combustion is self-sustaining with difficulty.

For a pyrotechnic composition, the fact of not having a stable and self-sustaining combustion at low pressure constitutes a major drawback when said composition is used in a gas generator for airbags, mainly for the following reasons:

- risk of extinguishment at very low pressure at the beginning or end of operation, due to a high value of the pressure exponent, which may require resorting to a co-charge in order to maintain the combustion of the main charge at low pressure. Thus, the gas generator is bulkier, less compact and therefore more expensive;
- risk of extinguishment at the end of operation (when the pressure in the chamber of the generator drops below the self-sustaining combustion pressure limit of the pyrotechnic composition), extinguishment that results in the presence of unburnt products, which do not contribute to the generation of combustion gas participating in the inflation of the bag according to the objective functional requirement. Furthermore, these unburnt products may gradually be degraded via a pyrolysis phenomenon under the effect of a residual high temperature in the combustion chamber. This slow degradation via pyrolysis results in the emission of bursts of gas that are difficult to control and sometimes solid particles of small size which cannot be captured by the filter. Such a phenomenon results in the appearance of fumes at the end of operation, which are prejudicial to compliance with the standards of

toxicity and of emission of breathable particles that are in force in the field (USCAR).

In such a context, the inventors desired to propose improved pyrotechnic gas-generating products, which are improved in that they simultaneously meet the following objectives:

- a moderate combustion temperature (close to 2100 K),
- a high gas yield (greater than 30 mol/kg),
- a limited content of solid particles generated during combustion,
- a good "ignitability",
- a high combustion rate at high pressure (greater than 35 mm/s at 20 MPa, greater than 40 mm/s at 50 MPa), and
- a combustion, with advantageous combustion rates, that is stable and self-sustaining at low pressure, ideally at atmospheric pressure, making it possible to avoid a risk of extinguishment of the charge during operation in generator.

Within the context of the present invention, the inventors have shown, more particularly with reference to the technical problem of improving the combustion at low pressure while maintaining a high combustion rate at high pressure, the great advantage in incorporating, in a limited content (from 1% to 5% by weight), in a composition containing a moderate amount of potassium perchlorate, at least one oxide, chosen from metal oxides, metalloid oxides and mixtures thereof, said at least one oxide having a melting point below the combustion temperature of the pyrotechnic product (in order to thus avoid any agglomeration effect of the combustion residues, which is prejudicial to maintaining a sufficiently high combustion rate at high pressure). Said at least one oxide, for the formation of a homogeneous pulverulent mixture (comprising mainly GN + BCN + KClO_4 + said at least one oxide (see below)) intended to be used with a view to the formation of a pyrotechnic product of the invention via dry route, is in the form of a pulverulent charge of micron-scale particle size (typically between 0.1 and 100 μm) and/or of high specific surface area ($> 20 \text{ m}^2/\text{g}$). These are customary characteristics for a constituent of this type.

The inventors therefore presently propose novel high-performance pyrotechnic products, for use in gas generators of "hybrid" type or of

entirely pyrotechnic type, which are particularly suitable for use in airbag systems for side application.

The compositions of the pyrotechnic gas-generating products of the invention (very particularly suitable for airbag applications) comprise:

- guanidine nitrate (as nitrogen-containing reducing charge),
- basic copper nitrate (as main oxidizing charge), and
- potassium perchlorate (as secondary oxidizing charge).

Characteristically: said potassium perchlorate represents between 8% and 20%, advantageously between 10.5% and 20%, of the total weight of said pyrotechnic product; and

said composition additionally comprises at least one oxide, chosen from metal oxides, metalloid oxides and mixtures thereof; said at least one oxide representing between 1% and 5% of the total weight of said pyrotechnic product and having a melting point below the combustion temperature of the pyrotechnic product.

The ingredients of the four types above (GN, BCN, KClO_4 and oxide(s) of the aforementioned type) generally represent more than 90% by weight of the composition of the products of the invention, very generally more than 95%, or more than 98%, or even 100%, by weight. The optional presence of additives, such as manufacturing auxiliaries (for example calcium stearate), is expressly anticipated.

Guanidine nitrate was chosen as a reducing agent for its thermodynamic properties (especially its gas yield), for the ballistic properties that it imparts to the pyrotechnic product, and for its rheoplastic behavior favorable to the use of the dry process for obtaining said pyrotechnic product. Said guanidine nitrate is particularly advantageous for pyrotechnic safety reasons and for this rheoplastic behavior highly suited to the use of compacting and optional pelletizing phases of the dry process, ensuring a good densification of the pyrotechnic composition while limiting the compressive stress to be applied. The manufacture of pyrotechnic products via the dry process generally comprises four main steps, which have in particular been described in patent application WO 2006/134311.

The potassium perchlorate is present, in the composition of the products of the invention, in a moderate content (from 8% to 20% by weight), very particularly with reference to the combustion temperature,

the "ignitability" and the combustion rate at high pressure that are targeted. It is advantageously present for at least 10.5% by weight.

It has been understood that the function of said at least one metal and/or metalloid oxide is not, as in the prior art (see in particular the teachings of patent US 6 143 102 and application US 2006/0016529 recalled above), to agglomerate the liquid copper particles during the combustion in order to form, during said combustion, a particulate gangue prejudicial to obtaining a high combustion rate at high pressure, but to ensure within a composition (containing a moderate content of KClO_4), the combustion temperature of which is greater than the melting point of said at least one metal and/or metalloid oxide, surprisingly:

- a stable and self-sustaining combustion at lower pressure than that of the compositions of the prior art,
- a combustion rate at low pressure that is higher than that of the compositions of the prior art;

the potassium perchlorate present within said composition being, for its part, essentially responsible for

- a high combustion rate at high pressure, close to that of the compositions of the prior art, and
- a pressure exponent over the whole of the pressure range equal to or lower than that of the compositions of the prior art.

In this way, the products of the present invention advantageously reconcile:

- a moderate combustion temperature (close to 2100 K),
- a high gas yield,
- a high combustion rate at high pressure, and
- a non-zero combustion rate at low pressure, or even at

atmospheric pressure,

with a "good" "ignitability" and without generating too many solid particles during the combustion.

Within the context of the present invention, an original use of metal and/or metalloid oxides (known as ballistic catalysts and/or agglomerating agents) is therefore proposed for improving the combustion at low pressure (see above).

Said at least one oxide, present in the composition of the products of the invention at at least 1% by weight, is therefore responsible for an

improvement in the combustion at low pressure. Its content is limited to 5% by weight, with reference, very particularly, to the gas yield and to the combustion at high pressure of said products.

In order to obtain the products of the invention, the necessary proportions of the aforementioned ingredients (constituents of said products) resulting in the desired properties (those of said properties which result from thermodynamic calculations: combustion temperature, gas yield, content of solid residues, oxygen balance and theoretical density, etc.) are therefore determined beforehand while ensuring that the condition relating to the melting point of the at least one metal and/or metalloid oxide present (melting point which must be lower than the combustion temperature of the product containing, in its composition, said at least one oxide) is met (then, the advantageous results, demonstrated by the inventors, are observed over combustion at low pressure).

The melting point of said at least one oxide present (of the oxide present or of each of the oxides present) in the composition of the pyrotechnic products of the invention is advantageously at least 50 K below the combustion temperature of said pyrotechnic product.

Preferably, said at least one oxide is chosen from silicon oxide (SiO_2), tungsten oxide (WO_3) and molybdenum oxide (MoO_3). Silicon oxide (SiO_2) is more particularly preferred.

Advantageously, the compositions of the products of the invention comprise, expressed as weight percentage:

- from 50% to 65% of guanidine nitrate,
- from 20% to 40% of basic copper nitrate,
- from 8% to 20%, advantageously from 10.5% to 20%, of potassium perchlorate, and
- from 1% to 5%, advantageously from 1% to 3%, of said at least one metal and/or metalloid oxide.

The products of the invention are therefore very advantageously obtained by a dry manufacturing process which comprises a first step of dry mixing the ingredients in powder form and a second step of compacting the pulverulent mixture obtained. These two steps are optionally followed by a third step of granulation, itself followed, if necessary, by a fourth step of forming, via pelletizing, of the granules obtained in order to obtain compressed products.

The products of the invention are therefore generally in the form of granules, pellets or blocks.

So as to facilitate the implementation of the pelletizing, by interfering as little as possible with the desired functional performances of the final product, an additive may be added, after the granulation phase. This additive is advantageously from the family of stearates. It preferably consists of calcium or magnesium stearate. The content added is less than 1% and preferably less than 0.5% (% by weight).

The products of the invention are very particularly suitable for being integrated into the pyrotechnic charge of a gas generator for airbags. They may constitute all or part of said charge.

According to another of its subject matters, the present invention relates to gas generators containing at least one pyrotechnic product of the invention. Said generators are perfectly suitable for airbags (see above).

It is now proposed to illustrate, in no way limitingly, the invention presently claimed. Compositions (of products of the invention) illustrating several variants of the invention are described and compared with examples of compositions (of products) from the prior art.

Figure 1 shows the curves of rate of (propagation of) combustion at low pressure for products of the invention and products from the prior art. Measurements were performed on the granules via the "strand burner" technique (see below).

Figure 2 shows the curves of combustion rate over a wide pressure range for products of the invention and products from the prior art. Measurements were performed on the pellets in a manometric bomb.

Table 1 below presents examples of compositions of products of the present invention, and also their associated performances. The compositions (products) were evaluated by means of thermodynamic calculations or from physical measurements obtained on granules or pellets manufactured from said compositions via the dry process of powder mixing – compacting – granulation – and optionally pelletizing.

As a function of the content of oxide incorporated, the content of the major constituents (GN, BCN and KClO_4) was adjusted in order to maintain an oxygen balance value close to -3%, so as to be able to directly compare the performances of the compositions from table 1.

The major constituents used in the compositions described in table 1 advantageously have a fine particle size, characterized by a value of the median diameter (D50) of around 12 μm for the guanidine nitrate, of around 3 μm for the BCN and of around 10 μm for the KClO_4 .

The metal or metalloid oxides used in the compositions of examples 1 to 4 are characterized by a melting point of around 1950 K (SiO_2), 1070 K (MoO_3) and 1750 K (WO_3). The silicon oxide has a specific surface area of 100 to 200 m^2/g , the molybdenum oxide has a median diameter centered about 10 μm and the tungsten oxide has a median diameter centered about 100 μm .

The compositions of examples 1 to 4 are constitutive of products according to the present invention, those of the reference examples (comparative examples A and B) are constitutive of products according to patent application FR 2 892 117 from the prior art.

Table 1

	Ref. A	Ref. B	example 1	example 2	example 3	example 4
Composition of the products	% by weight					
KClO ₄	10	8	11.8	11.6	11.7	11.7
guanidine nitrate	58.2	57.2	58.2	57.3	57.6	57.6
basic copper nitrate	21.8	34.8	28.5	28.1	28.2	28.2
SiO ₂	0	0	1.5	3	0	0
MoO ₃	0	0	0	0	2.5	0
WO ₃	0	0	0	0	0	2.5
Thermodynamic calculations						
Combustion temperature at 20 MPa (K)	2068	2041	2077	2059	2065	2077
Gas yield at 1 bar and 1000 K (mol/kg)	30.9	30.7	30.7	30.2	30.4	30.4
Content of solid residues at 1 bar and 1000 K (%)	22.9	23.3	23.6	24.7	22.2	24.3
oxygen balance (%)	-3.1	-3.1	-3.1	-3.0	-3.0	-3.0
theoretical density (g/cm ³)	1.869	1.889	1.858	1.866	1.878	1.884

Ballistic performances measured									
Low combustion pressure limit (bar)	5	3.5	< 1 (*)	< 1 (*)	1.5	2.5			
Combustion rate at atmospheric pressure (mm/s)	0	0	0.6	1.1	0	0			
Combustion rate at 20 MPa (mm/s)	39.5	36.6	39.2	36.4	35.7	35.7			
Combustion rate at 50 MPa (mm/s)	48.6	46.6	44.8	42.0	44.4	45.0			
pressure exponent	0.21	0.24	0.13	0.13	0.23	0.24			
Appearance of the combustion residues	no agglomerated residues in the form of a backbone of the pyrotechnic block								
Mechanical strength and densification on pellets (**)									
Porosity (%)	1.1	1.3	< 1	< 1	1	0.9			
Radial crushing strength (kP)	15.8	15.3	16.4	17.6	16.2	16.5			

(*) non-zero combustion propagation rate at atmospheric pressure

(**) pellets having a diameter of 6.35 mm and a thickness of 3 mm

For each of the products from table 1, the combustion pressure limit was measured on granules via the "strand burner" technique (firings in a pressurized vessel). For this, the granules are introduced into a straw having a diameter of 7.4 mm, which is placed in a chamber having a capacity of 5 liters that is pressurized under an inert atmosphere (N_2). The ignition is carried out using a hot wire, then the measurement of the rate of propagation of the combustion is performed using 2 fusible wires lodged in the straw and spaced 100 mm apart. The firings were carried out at 20°C for various vessel pressurization values until the non-ignition of the granules of each composition was observed.

For each of the products from table 1, the combustion rate (V_c) was measured on pellets by means of firings carried out in a manometric bomb. The firings were carried out for various charge density values (35 kg/m^3 to 175 kg/m^3) in order to establish the curve $V_c(P)$ over a wide pressure range.

The results from table 1 indicate that the compositions of examples 1 to 4 according to the invention have:

- advantageously, a maintenance of the performances, in terms of density, combustion temperature and gas yield, compared to the compositions of comparative examples A and B. These performances are important because they play a major part in the expected function of the composition (inflation power);
- a good aptitude for densification, as the low porosity values measured on pellets indicate. This aptitude for densification is important for the manufacture of compacted granules and also for the manufacture of pellets, the geometry, diameter or thickness of which may be easily adapted depending on the envisaged application. It also makes it possible to be able to apply a minimum compressive stress during the processing of the product via pelletizing, which reduces wear of the tools and the pyrotechnic risks during compression; and
- result in pellets being obtained that have a satisfactory mechanical strength. The incorporation, at a moderate content, of an oxide of SiO_2 , MoO_3 or WO_3 type does not degrade the

mechanical strength of the pellets, as the radial crushing strength values indicate.

The low combustion pressure limit values indicated in table 1 and the combustion rate curves at low pressure from graph 1 show that the incorporation, at a moderate content (between 1.5% and 3% in the examples), of an oxide of silicon oxide, molybdenum oxide or tungsten oxide type makes it possible to significantly decrease the combustion pressure limit value relative to that of the reference compositions A and B. Among the compositions of examples 1 to 4, the composition of example 2 formulated with 3% of silicon oxide has the most notable improvement since it has a non-zero combustion rate value at atmospheric pressure and, generally, the highest combustion rate over the pressure range extending from 0.1 to 1 MPa.

With reference to figure 2, the ballistic characterization in a manometric bomb carried out on pellets manufactured from compositions cited in table 1 show that the compositions of examples 1 to 4 have a combustion rate that remains high enough over the high-pressure range extending from 20 to 50 MPa.

The product of example 1, formulated with 1.5% of silicon oxide, offers the best compromise of performances between combustion temperature, gas yield, combustion pressure limit and combustion rate at high pressure. This product especially has the great advantage of maintaining a non-zero combustion rate at atmospheric pressure. The incorporation of silicon oxide at a content of 3% according to the composition of example 2 appears even more beneficial to combustion at very low pressure, but in return generates a reduction in the combustion rate at high pressure. These results indicate that the silicon oxide is advantageously incorporated up to a content of 3% in order to preserve a sufficient ballistic performance at high pressure over the range 20 to 50 MPa.

Among the various oxides tested, a beneficial reduction of the pressure exponent was observed for the products of examples 1 and 2, formulated according to the present invention with silicon oxide.

Due to the fact that the melting point of the oxide incorporated (SiO_2 , MoO_3 or WO_3) remains below the combustion temperature of the composition, no combustion residue, agglomerated in the form of a backbone of the pyrotechnic block, that is to say having the initial form of the pellet, is observed, as is customarily the case for compositions based on BCN incorporating a high melting point refractory oxide such as aluminum oxide.